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Separation of Hydrogen Isotopes by a Flowing Bed Process

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CFFTP will sponsor research, development and studies to extend existing experience and capability gained in handling tritium as part of the CANDU fission program. It is planned that this work will be in full collaboration and serve the needs of international fusion programs.

SEPARATION OF HYDROGEN ISOTOPES BY A FLOWING BED PROCESS

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TABLE OF CONTENTS

LIST OF FIGURES

Figure

LIST OF TABLES

Table

1.0 **ABSTRACT**

Results of an experimental study on a flowing bed process for continuous hydrogen isotope separation are presented. Separation performance was low with a 25% by weight palladium on alumina adsorbent, resulting in a high tritium inventory. In addition, significant breakdown of the solid adsorbent occurred as it recirculated through the process equipment and the product streams were contaminated by the adsorbent carrier gas. Due to these problems, this flowing bed process is predicted to be uneconomic for a full scale plant.

2.0 EXECUTIVE SUMMARY

It has been suggested that processing of up to 200 L/d of the light water coolant of fusion power plants may be required to remove tritium. Cryogenic distillation technology has been demonstrated, but the presence of liquid tritium in the distillation process results in a significant in-process tritium inventory. An alternative process based on gas adsorption but similar to distillation was investigated in the present study. This flowing bed process utilized a bed of solid adsorbent which moved down the column while gaseous hydrogen isotopes flowed up the column. The least adsorbed gas component flowed to the top of the column while the more strongly adsorbed isotope was carried to the bottom of the column. The main objective was to generate data to allow the technical and economic feasibilities of the process to be evaluated.

Evaluation of several adsorbents including metals that form hydrides showed molecular sieve and a palladium based adsorbent to be most promising. Palladium (25% by weight) on alumina was finally chosen for study to avoid operation at liquid nitrogen temperatures required with molecular sieve, and because it promoted the transformation of HT species to protium and tritium. An initial granular alumina proved to be too friable and was replaced by a stronger spherical alumina substrate. This latter material was heat treated to increase its pore size.

Tests were carried out on a bench scale apparatus which contained all the essential components of a full scale plant. Solids return to the top of the column was effected by nitrogen lift gas allowing continuous operation of the process over many hours. However, it was necessary for nitrogen to be present in the product streams to avoid process emissions. Solids velocity down the column was adjustable over a wide range by adjusting the intensity of a vibrator and excellent plug flow was obtainable thereby reducing back mixing and increasing separation efficiency.

Separation performance tests on hydrogen/deuterium mixtures were carried out by varying several factors including the column hydrogen isotope feed rate, the feed composition, the bottom product take-off rate and the solids flow rate down the column. The best performance was obtained at high solids velocity down the column, at low top product (D_2) removal rates and with high deuterium concentrations in the feed. However, the amount of palladium required was about 2.5 times that found by previous workers who investigated pure palladium black in a simulated moving bed system. Additional tests showed that the transfer process was considerably slower in the impregnated alumina as compared to pure palladium probably because of slow diffusion in the pores of the alumina even though the pore diameter had been increased by heat treatment.

Attrition rate tests on the palladium impregnated alumina showed that about 15% of the material in a full scale column would have to be replaced each year resulting in significant costs. The large amount of palladium required for the separation resulted in an adsorbent cost which made the present configuration of the process uneconomic for the above application. Furthermore, the inventory of tritium was estimated to be at least an order of magnitude greater than for a cryogenic distillation process due to the large amount of palladium required to effect the separation.

3.0 INTRODUCTION

It has been suggested/1/ that cooling in fusion power plants will be carried out with light water (H_2O) which will become tritiated. Processing of up to 200 L/day of this water will be required to remove tritium present at 50 Ci/L of liquid H_2O ($\approx$ 15 μL T_2/L of hydrogen). Tritium removal is also required from the heavy water moderator and primary coolant (D_2O) in Ontario Hydro's CANDU* stations. Process options for detritiation include electrolysis of the water to produce a gas mixture of hydrogen isotopes which can then be separated by cryogenic distillation. However, the Darlington Tritium Removal Facility will use isotopic exchange. Deuterium gas exchanges with tritium in D_2O vapor in the presence of a catalyst. The mixture of D_2 and DT is then separated by distillation at about 20 K. Top and bottom product streams are expected to contain 99.9% T_2 and 0.3 μL/L T_2 respectively from a feed composition of 15 μL/L T_2.

Cryogenic distillation of hydrogen/tritium mixtures is a mature technology and process optimization is presently being investigated at the Tritium Systems Test Assembly (TSTA) in the Los Alamos National Laboratories. The presence of liquid tritium in the distillation process results in an undesirable significant inventory of radioactive material. Efforts are underway at TSTA to reduce this. Also, cryogenic distillation requires that expansion tanks be provided in the event of failure in the supply of the cryogenic fluid.

3.1 Flowing Bed Process Description

It was anticipated that it may be possible to avoid significant tritium inventories associated with liquid tritium using a process based on gas

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* CANDU = Canadian Deuterium Uranium

adsorption but similar to distillation. The flowing bed process utilizes a bed of adsorbent which moves down a column while the gas mixture is made to flow upwards. Preferential adsorption of one component of the gas mixture occurs on the adsorbent. The most volatile (least adsorbed) component goes to the top of the column and the least volatile to the bottom of the column to the "reboiler". The process is similar to distillation except that the liquid phase flowing down the distillation tower is replaced by solid adsorbent particles and these must be returned to the top of the column.

3.2 Previous Work

Work on separating protium/deuterium mixtures with this process has been carried out by Basmadjian/2/. He worked with charcoal at 77 K and a large charcoal feed bin to circumvent the requirement of solids return to the top of the bed. Similar studies were carried out by Clayer et al/7/ who utilized pneumatic transport for solids return. These workers utilized silica gel as the adsorbent for separating mixtures of protium and deuterium. However, it was still necessary to run the process at cryogenic temperatures (77 K). This increases the equipment required since gas storage vessels must be provided for use in the event of cryogenic system failure.

A recent Russian study, Andreev et al/3/, reported results on a simulated moving bed utilizing pure palladium particles as the adsorbent. The advantage of this adsorbent is that the process can be run at about room temperature except for desorption in the "reboiler" at the bottom of the column taking place at about 150°C. The moving bed was simulated by having several interchangeable short sections in the column. The feed of protium and deuterium was introduced at the bottom section and allowed to flow until the palladium in the top section became saturated. The bottom section was then removed and heated to desorb the bottom product. Since the feed section was the same as the bottom section this produced a simulation of the top portion only of a real column. The section which had been heated to desorb bottom product was then cooled. Finally, it was manually returned and attached to the top of the column and the feed gas flow was restarted. From a knowledge of the separation factor (α)*, determined in previous experiments/4,5/, which describes the equilibrium curve of gas compositions versus adsorbed material composition, Andreev et al/3/ determined the height of a transfer unit (HTU) to be 2 to 3 cm. This translates to about 12 g Pd per stage for a column of unit area (for a 25% palladium on alumina adsorbent of bulk density 1.25 g/cm^3, this is equivalent to an HTU of 38 cm). Preliminary costs estimated at the start of this study and presented in Appendix D indicated further investigation of palladium should be carried out.

3.3 Objective

As described above, several adsorbents may be used in the flowing bed process including palladium, molecular sieve, silica gel and several metals that form hydrides. In addition, the overall process has been run with continuous solids return by Clayer et al/7/ only and these workers investigated silica gel at cryogenic temperatures. The present study was initiated to:

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* The separation factor α is defined as:

$$\alpha = \frac{\left(\dfrac{\text{(moles of least adsorbed gas)}}{\text{(moles of most adsorbed gas)}}\right)_{\text{gas phase}}}{\left(\dfrac{\text{(moles of least adsorbed gas)}}{\text{(moles of most adsorbed gas)}}\right)_{\text{solid phase}}}$$

(a) investigate "proof of principle" of a flowing bed system to detritiate fusion reactor coolant streams; and

(b) generate design data to allow the technical and economic feasibilities of the process to be evaluated.

Individual tasks included selection of adsorbent, development of solids handling systems, design of the bench scale apparatus followed by assembly and testing of the bench scale system.

4.0 EXPERIMENTAL MATERIALS AND EQUIPMENT

Although palladium black was used by Andreev et al/3/ it is not a suitable material for a practical system in which solids conveying is required. Also, it was believed that the interior of pure particles would be poorly utilized if diffusion was slow.

As described in Appendix B on adsorbent selection, alumina impregnated with 25% by weight palladium was selected as the adsorbent. This allowed design of the bench scale system for operation at near ambient temperatures. Also, from Appendix D, the full scale column diameter was estimated at 12.5 cm (four units operating in parallel for a 200 L/d water detritiation plant). It was believed that 5 cm would be a suitable diameter for a pilot scale unit. Similarly, the diameter of the bench scale unit was estimated to be 2 cm. This translates to a scale up factor of six which is in the acceptable range for gas/solid systems. A schematic of the bench scale flowing bed apparatus is shown in Figure 1 and details are presented in Appendix B.

The bench scale column was 2 cm in diameter and 1.45 m long due to a ceiling height restriction. The hydrogen isotope feed port was located about mid-way along its length. Solid adsorbent movement down the column was controlled by the amount of solids feed gas (N_2) introduced at the bottom of the column or by a vibrator. Solids velocity down the column was adjustable by varying the vibration intensity. The hydrogen isotope mixture sorbed on the palladium was removed in the reboiler at the bottom of the column by heating and flushing upwards with nitrogen. This nitrogen was initially supplied at a nitrogen purge port. However, this port was removed after it was found that the high pressure in the nitrogen solids lift gas provided sufficient flow for purging up the reboiler leg. The adsorbent was returned to the top of the column with nitrogen lift gas. Narrow seal legs were placed at the top and bottom of the column to reduce the amount of nitrogen entering the column.

The poor separation performance described below resulted in the work being carried out only on the bench scale and with hydrogen/deuterium mixtures only.

5.0 RESULTS AND DISCUSSION

5.1 Column Temperature Profile

The highest temperature in the column was at the reboiler which was heated electrically to about 190°C. The next highest temperature (approximately 70°C when the column itself was not being heated to investigate the effect of high temperature operation) was near the bottom of the top seal leg. There, the recirculated solids contacted the hydrogen flowing up the column. The coolest area was near the feed port (approximately 50°C) while the temperature at the bottom port was higher (approximately 60°C) due to hot nitrogen from the reboiler flowing upwards to strip off hydrogen adsorbed on the palladium.

5.2 Column Pressure Profile and Product Flow Control

Proper operation of the moving bed column required careful control of the column pressure profile. It was desirable that both top and bottom products contain a small amount of nitrogen (~5%) as a result of flow from the disengager to the top product port and from the N_2 solids lift gas port to the bottom product port. Reverse flow would result in product loss and a contaminated vent stream. Therefore the desired pressure profile was that the pressure should be greater at the N_2 solids lift gas port than at the bottom product port and greater in the solids disengager than at the top product port. The pressure in the column was dependent on the bottom product flow rate, the solids flow rate down the column, the solids disengager pressure, the solids lift gas rate and the hydrogen isotope feed rate.

The top product flow was not restricted allowing top product pressures close to atmospheric. The pressures at the disengager and at the solids lift gas port at the bottom of the moving bed column were adjusted to be higher than at the top and bottom product ports, respectively. This was accomplished by restricting the flow of lift gas at the cyclone exit which prevented hydrogen isotopes from being present in the solids lift gas effluent but resulted in undesirably high nitrogen levels in the bottom product (> 5%) and in the D_2-rich top product (as much as 90% N_2).

Taking off too much bottom product (by not restricting the bottom product outlet valve) resulted in no hydrogen in the top product. This was especially true at high solids velocity down the column when all the hydrogen feed was adsorbed at the feed port with the high temperature zone occurring there. As the bottom product flow was restricted, the pressure increased at the bottom of the column and the high temperature zone climbed up the column. Since only a small deuterium-rich top product flow was desirable due to the small amount of deuterium in the feed, a fine control was required to ensure just the right amount of top product flow.

As described above, restricting the bottom product flow resulted in higher bottom product pressures. Similarly, solids movement down the column produced a pumping effect resulting in increased bottom product pressure. As the bottom product pressure increased, its nitrogen content decreased and it was often necessary to increase the solids lift gas pressure to maintain adequate nitrogen levels. This was done by partially closing the valve at the cyclone exit thereby increasing the top disengager pressure and the solids lift gas pressure and forcing the required amount of nitrogen up the reboiler. However, increasing the top disengager pressure by partially closing the valve at the exit of the cyclone resulted in a very large amount of nitrogen flowing down the top seal leg into the top product. Alternatively, the solids lift gas pressure at the bottom of the column could have been increased by increasing its flow rate. The disadvantages include wastage of nitrogen and attrition in the lift line offsetting the advantage of a lesser amount of nitrogen in the top product. Reduction of the amount of nitrogen in the top product by increasing the length of the top seal leg was not attempted.

At hydrogen isotope feed flow rates greater than 300 - 400 mL/min and low solids velocities down the column (approximately 2.5 cm/min), the pressure profile in the column was incorrect with the pressure at the feed port being greater than the pressure at the bottom product port. Increasing the solids velocity down the column corrected the overloaded condition.

5.3 Solids Flow Control

The particle size of alumina chosen for impregnation with palladium had to be small to prevent plugging with the bench scale apparatus. Small particles were also favoured because they allowed rapid exchange through diffusion of gases over short distances in and out of particles. Also, rapid heating of the internals was possible in the reboiler. However, the strength of the alumina decreased with decreasing particle size. Consideration of these factors led to a diameter in the range 0.5 to 1.2 mm being chosen for the adsorbent in the present work.

Plug flow down the column was desired. Solids containing adsorbed material of a given composition in the lower portion of the column would then not backmix and adversely affect the gas composition at the upper portion of the column. Tests were carried out with dyed layers of particles to investigate conditions for plug flow of solids. Figure 2 shows that a layer of particles increased in length about four to five times as it travelled down the full length of the column when the particles were sand and a nitrogen purge was used at the bottom seal leg. The nitrogen purge was discontinued and excellent plug flow was obtained for spherical and irregular Al_2O_3 granules. However, for gas induced solids movement, poor control was experienced with the flow either stopping or being too fast, ie, low flow rates were not obtainable although plug flow was. Conversely, excellent plug flow was obtained with vibration induced solids movement over a wide range of solids flow rates and this method was used for the generation of separation performance data.

The solids flow rate was significantly affected by the slope of the crosspiece at the lower end of the seal leg. Tilting downwards caused increased (more readily obtained) downflow at lower vibration intensities. The spherical alumina beads had an angle of slide of about 35° and a 20° tilt was used for the crosspiece. The upper limit of the flow rate was determined by the restriction at the junction of the solids disengager cone and the top of the small diameter upper seal leg which did not run full of solids above this rate.

5.4 Solids Attrition

Solids attrition and breakdown were investigated in two tests. In the first screening test the effect of hydriding/dehydriding on the friability (tendency to powdering) of the 25% Pd on Al_2O_3 adsorbent was investigated. Several grams of the adsorbent were hydrided by passage of hydrogen until cool again and then heated to approximately $200^\circ C$ to dehydride them. After zero, five and ten cycles, one gram samples were taken and vigorously shaken in a small mill similarly to autogenous grinding practice. No difference was found in the percentage of fines produced after 45 min of shaking between material which had not been hydrided and that which had undergone up to ten hydriding cycles. This screening test allowed continuation of the test program.

In the second test, the rate of breakdown of the solids during continuous recirculation was studied. Preliminary investigations showed that irregularly shaped solids exhibited rapid breakdown characteristics especially during the initial period of recirculation and gradually became rounded. Hence, spherical beads were chosen for the shape of the alumina substrate. It was also found that most of the breakdown was occurring in the solids lift line. After approximately 40 hours of testing with the 25% Pd on alumina adsorbent beads, significant black dust was visible in the dust impactor downstream of the cyclone and the vent line. The average loss rate per hour was 0.05% of the contents of the system (approximately 675 g Pd/Al_2O_3) which translates to about 1 gram of fines for every 10 kg of solids recirculated at approximately 12 cm/min solids velocity. There was also evidence that the procedure for impregnating the palladium onto the alumina substrate had weakened the alumina or that the palladium impregnated surface was softer since a loss rate of about 0.03%/h was found for unimpregnated beads.

5.5 Separation Performance

The experimental data on separation performance are given in Table 1. Calculation methods are given in Appendix C. Performance tests on separating hydrogen/deuterium mixtures were carried out by varying several factors including (a) column feed rate (1000, 300, 100 and 0 mL/min corresponding to total reflux), (b) feed composition (1% D_2 and 30% D_2 in H_2), (c) bottom product take-off rate (about 20 to 80% of feed rate), (d) solids flow rate down the column (2.3 to 14 cm/min), and (e) carrier gas (nitrogen and helium).

Steady state was established about two hours after start-up with the column preloaded with hydrogen isotopes from the previous day's test. At the feed port, the 1% D_2 in H_2 feed gas was rapidly converted to 2% HD by the palladium.

At a 300 mL/min feed rate and 2.4 cm/min solids velocity down the column, the separation was negligible. Figure 3 shows the separation on reducing the feed rate to about 110 mL/min. At low bottom product take-off rates, the top product composition did not change significantly as the bottom product take-off rate was increased. However, significant increases in the D_2 content of the top product were obtained as the bottom product take-off rate approached the feed rate, ie, as the top product flow was reduced. This was one of the two most important factors influencing separation efficiency. This is expected since if the feed contains a small amount of deuterium and a large amount of gas is removed in the top product then the separation will be low. This is similar to operation at low reflux ratio. At the same time, however, taking off bottom product at high rates resulted in a bottom product D_2 content which was very similar to that of the feed stream, eg, tests 44 and 28(i). Significant improvements were also apparent if the solids velocity down the column was increased from 2.4 to 9.0 cm/min but the separation was still relatively small. It is believed that the increased separation resulted from the increased "liquid" flow down the column. This produced increased gas flows up the column due to reboiler operation. The practical upper limit for the present apparatus was about 12 cm/min to avoid breakage of the glass apparatus and to allow time for heating of the solids in the reboiler.

A single transfer unit may be defined as giving a D_2 enrichment in the gas phase equal to the average driving force (actual D_2 concentration - concentration in gas in equilibrium with concentration on solid) producing this enrichment (see Appendix C). The number of transfer units obtained in the top section of the column was in general greater than for the bottom section of the column indicating that long lengths of bottom section are required for significant reduction of the D_2 content. The height of a transfer unit (HTU) was significantly greater than the 38 cm value (approximately 12 g Pd/stage/cm^2) estimated from the data of Andreev et al/3/.

In one test (test 33), the column was fed with gas containing 30% D_2 and the top and bottom products contained 52 and 24% D_2, respectively. The number of transfer units was significantly greater than at low D_2 content showing easier separation at higher feed concentrations but still less than expected from the Russian data. Operation at total reflux with no feed showed no significant change in bottom product composition but this result is tentative since it was necessary to have nitrogen flowing up the column to the disengager under these conditions. For capital cost estimation purposes, an average HTU of 100 cm was assumed since it increases with increasing D_2 concentrations.

As shown in Table 4 (test 44), at a feed flow rate of 1010 mL/min, the bottom product pressure was lower than the feed pressure. This indicated that overloading of the column was occurring. The pressure profile was acceptable at a feed rate of 350 mL/min. For capital cost estimation purposes, therefore, the capacity of the column was considered to be about 750 mL/min or 240 $mL/min/cm^2$. This is about 20% less than the 300 $mL/min/cm^2$ capacity calculated at the start of this study from the data of Andreev et al/3/.

5.6 Low Separation Performance Investigations

Helium was substituted for nitrogen as the carrier gas to investigate (test 31) whether adsorption of nitrogen by the alumina contributed to the low separation observed. The data of test 31 may be compared to those of test 30 performed with nitrogen. Although conditions of bottom product flow rates and solids velocity down the column are somewhat different, a significant reduction from 280 to 124 was observed in the height of the transfer unit for the bottom half of the column. It is tentatively concluded that nitrogen adsorption does contribute to the low separation observed.

Additional tests were carried out to investigate under the most favourable conditions what was the minimum length of column required to significantly reduce the deuterium content of the adsorbent used in the present study. The first step of the procedure was to load a small 5 cm long bed with 0.01 mole fraction D_2 to simulate conditions at the feed port of the moving bed system. The stationary bed was then flushed with pure hydrogen or hydrogen containing very little deuterium to simulate the processes occurring in the bottom half of the column under optimum conditions. As shown in Table 3, the column lengths required to reduce the mole fraction of D_2 in the bottom product to 0.005 and 0.001 were about 23 cm and 30 cm, respectively. These values, therefore, represent the shortest bottom section lengths required for producing bottom product of the compositions given above. These data may be compared to test 25 (i - iii) data obtained at a similar flushing (solids) velocity. It is seen that the D_2 content of the bottom product was significantly higher (about 0.0096) although the length of the bottom section was greater (about 75 cm).

Also shown in Table 3 are results obtained for a bed containing a mixture of pure palladium black and alumina spheres. It is seen that at similar flushing rates, the effluent D_2 content could be reduced to 0.001 mole fraction in 8 cm as compared to 30 cm required with the 25% Pd/Al_2O_3 adsorbent used in the present study. It is possible that diffusion in the pores of the substrate is responsible for the slow rates observed with the Pd/Al_2O_3 adsorbent and the large values for the HTU observed in the moving bed column. Also, backmixing may be greater in the moving bed column since the bed is not as compact as a stationary bed due to its downward motion.

5.7 Adsorbent Cost Estimation and Tritium Inventory for Full Scale Plant

5.7.1 Adsorbent Cost

The data obtained in this study with the bench scale flowing bed apparatus were used to estimate the diameter and height of a full scale plant to detritiate 200 L/d of light water containing 50 curies of tritium per litre. The calculation method is presented in Appendix C and the result is more accurate than the estimate which was made at the beginning of this study (see Appendix D. It was assumed that the coolant stream would be electrolysed to produce an H_2/HT gas stream to be treated by the moving bed process. This gives the minimum amount of hydrogen to be processed as compared to vapor phase catalytic exchange. Hence, the size of the process equipment will be relatively smaller and so will be the amount of expensive adsorbent required. Top and bottom product streams were assumed to be 999×10^3 μL/L T_2 (99.9%) and 0.3 μL/L T_2, respectively, for a 15 μL T_2/L feed gas stream. Additional conditions are presented in Appendix C.

The column diameter was calculated to be 30 cm and this allowed operation above the minimum reflux limit. Separation factors reported by Andreev et al/4/ were used and the effect of concentration on the separation factor was taken into account. The number of transfer units for the desired separation was then computed to be 33. The height of a transfer unit for hydrogen and tritium separation was assumed to be the same as the 100 cm found for hydrogen and deuterium in the bench scale work. The data of Andreev et al/5/ suggest it may be 50% larger. Assuming a palladium cost of $4,800 Cdn/kg ($150 Cdn/oz) and a 25% processing cost during adsorbent manufacture, results in a total adsorbent cost of about $5 M. The processing cost was increased from 15% previously assumed because of additional heat treatment required. This total cost is significantly greater than had been suggested/8/ as necessary to compete with cryogenic distillation. Based on the attrition data, it will also be necessary to replace 15% of the column per year at a cost of about 0.75 M$/yr.

5.7.2 Column Tritium Inventory

The compositions of the gas and solid phases were calculated from the separation factor at every 100 cm interval (each HTU value) up the moving bed column. The capacity of the palladium was measured to be about 100 mL H_2/g for H_2 and assumed to be the same for a mixture of isotopes. This resulted in a tritium inventory for a full scale plant of about 2 kg (20 MCi). This is significantly greater (about 40 times) than the inventory for a cryogenic distillation unit and its large value is due to the large height of a transfer unit found in these experiments.

6.0 CONCLUSIONS

1. The technical feasibility of the overall flowing bed process was demonstrated with continuous hydrogen isotope feed and product removal and continuous solids return to the top of the column. However, it was necessary for nitrogen to be present in both top and bottom products to avoid product gases in the solids lift gas vented to the atmosphere. Vibration induced solids movement produced excellent plug flow of the adsorbent down the column and it was possible to control the adsorbent velocity over a wide range.

2. The initial substrate material chosen for impregnation with 25% palladium on alumina had relatively large pores but was too friable. A substitute

spherical alumina exhibited improved resistance to powdering but the pore size was significantly smaller even after heat treatment. The majority of the breakdown occurred by mechanical action in the solids lift line as opposed to the main column. Limited tests showed a negligible effect of hydriding/dehydriding on the friability. However, attrition rate data indicate that 15% of the adsorbent would require replacement every year due to powdering.

3. The height of a transfer unit (HTU) was about 100 cm or about 30 g Pd/stage/cm^2 which is about 2.5 times that found by previous workers with pure palladium particles. The performance was better at high solid adsorbent flows down the column due to increased refluxing and at low top product take-off rates due to the small amount of deuterium in the column feed. The separation appeared easier at high feed concentrations, also.

4. The large value of the height of transfer unit resulted in a full scale column inventory for tritium which was over an order of magnitude greater than for a cryogenic distillation unit.

5. The large value of the transfer unit resulted in costs for the palladium based adsorbent which significantly exceeded the guidelines of a previous study. Therefore, this process in the present configuration of flowing Pd/Al_2O_3 adsorbent is considered to be uneconomic for the present application.

6. Flushing tests on a small stationary bed of impregnated alumina and one with pure palladium showed that the transfer process was considerably

slower in the impregnated material probably due to slow diffusion in the pores.

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APPENDIX A

Adsorbent Selection and Properties

A.1 Adsorbent Selection

Several adsorbents were evaluated at the start of this study with respect to the capital and operating costs expected for an environmentally acceptable and safe operation. Factors affecting capital cost included: (a) separation factor which determines column height; (b) adsorbent capacity for hydrogen which determines column diameter; (c) initial adsorbent inventory in column; (d) isotopic equilibration allowing conversion of HT to H_2 and T_2; (e) operating temperature; (f) operating pressure; (g) availability of suitable adsorbent geometry; and (h) provision of safety/clean-up equipment. Similarly, operating costs were primarily affected by resistance to poisoning, sintering and powdering, and also by the operating temperature.

The costs of flowing bed systems for various sorbents are estimated in Table 4. A relatively lower cost is attributed to the palladium column because of the high separation factor (2.1) for protium/deuterium mixtures as compared to 1.2 for molecular sieves and uranium, about 1.1 for vanadium and about 1.05 for FeTi. Conversely, the low capacity of palladium for hydrogen (100 mL/g Pd) is reflected by the high equipment cost for a larger diameter column. Similarly, because of its precious metal nature, a very high cost was estimated for palladium required to fill the column. Molecular sieve does not promote the reaction, $2\,HT \rightarrow H_2 + T_2$. Hence, additional equilibration equipment will be required for effective separation resulting in increased costs. Similarly, operation of molecular sieves at cryogenic temperatures will require more complex equipment resulting in high capital costs. Operating costs will also be high due to the liquid nitrogen requirement. A low cost was estimated for operation with palladium since operating temperatures are near ambient while, for example, temperatures greater than 400°C are required in the reboiler for uranium. Also, operating at about atmospheric pressure and a temperature at which the plateau occurs in the gas phase pressure vs solid phase composition curve would require cooling water or glycol for vanadium and ferrotitanium. Both alumina and molecular sieves are available in spherical form and size suitable for pneumatic conveying. Vanadium, uranium and ferrotitanium would require additional costly processing. Similarly, impregnation of palladium on the alumina is expected to be costly. High costs were attributed to vanadium and molecular sieves since tritium is the more strongly adsorbed species and will move to the bottom of the column. This increases the potential for carrier gas contamination. Oxygen poisoning of uranium, vanadium and ferrotitanium is expected to increase costs as is the brittle nature of their hydrides which suggests significant adsorbent makeup would be required.

Overall costs were estimated by allocating values in the range one to five for the descriptors, very low, low, average, high and very high. Although the error band is probably large, the results of Table 3 suggest that 25% palladium on alumina and molecular sieves are the more promising adsorbents. Palladium was chosen for further work because the results for operation with molecular sieve was expected to be similar to those obtained with silica gel and the required equipment was expected to be more complex due to operation at low temperature.

A.2 Properties of the Adsorbent Studied

Initial samples of adsorbent supplied by a catalyst manufacturer were made from crushed 1/8" cylindrical extrudates of alumina. Scanning Auger microprobing indicated that the palladium concentration averaged over areas of diameter 0.1 μm varied between 7 and 35% by weight over a line in a section in the interior of an impregnated particle. Also, at one spot on an impregnated particle, the palladium concentration fell from about 50% to 10% by weight over a distance of 3 μm inside the particle. For this material, the substrate had a pore volume of about 0.45 cm^3/cm^3. A bimodal pore size distribution was evident with peaks at 0.76 μm diameter and 0.22 μm diameter.

Because of significant powdering of the above adsorbent substrate during transportation around the flowing bed apparatus, a search was initiated for a material of pore diameter, pore volume and surface area similar to the above substrate but of spherical shape and improved powdering resistance. A spherical chi-alumina was found but required heat treatment to 900 - 950°C for two hours at about 70% relative humidity to increase the pore size. The pore volume that was finally accepted for further investigation was 0.38 cm^3/cm^3 and the pore size was in the range 0.07 to 0.01 μm (0.0125 μm average). While this size was significantly less than the previous values, it was larger than the 0.01 to 0.005 μm used in automotive applications. Other adsorbent properties included a palladium content of 25% by weight determined by atomic absorption spectrometry, a particle density of the unimpregnated alumina substrate of 1.56 g/cm^3, a particle density of the impregnated material of 2.1 g/cm^3, a particle diameter in the range 0.6 to 1 mm, a surface area of about 100 m^2/g, a bulk density of unimpregnated substrate of 0.82 - 0.92 g/cm^3, and a bulk density of impregnated material of 1.21 - 1.31 g/cm^3.

The bulk density of pure palladium which was used during investigations on reasons for poor performance of the moving bed process was 4.6 g/cm^3 for coarse material (<60 mesh, 250 μm).

APPENDIX B

Experimental Equipment and Procedure

B.1 Flowing Bed Column

The apparatus including the 2.0 cm diameter flowing bed column was constructed mainly of glass. The height of the column was restricted to 1.45 m because of a ceiling height restriction. The feed port was located about mid-way along the column length with the top section of the column being 0.70 m long and the bottom section being 0.75 m long. The feed, top product and bottom product ports were sloped upwards to retain solids in the column. At the top of the column a seal leg was installed to minimize the flow of gas into the column from the solids disengager. It was 0.7 cm internal diameter by 20 cm long.

Thermocouples were introduced at these locations as were pressure transducers or gauges for monitoring the pressure profile over the column. The hydrogen isotope feed consisting of 1% D_2 in H_2 was metered into the column by a calibrated mass flow controller. Rotameters which exhibit low pressure drops were used at the top and bottom products streams to indicate constancy of flow. Actual flow measurement was carried out with a soap bubble flow meter since the composition of nitrogen carrier gas, hydrogen and deuterium was variable and rotameter calibration for many compositions was not practical. The compositions of the feed, top and bottom products were determined by a quadrupole mass spectrometer. The spectrometer also indicated when all oxygen was purged from the system during startup with a nitrogen purge. Shutdown was accomplished by stopping the hydrogen isotope feed stream and continuing solids recirculation for hydrogen desorption. Following this, all ports were closed to reduce entry of oxygen and the catalytic production of water.

B.2 Reboiler/Bottom Seal Leg

The hydrogen isotope mixture sorbed on the palladium was removed at the bottom of the column by heating and flushing upwards with nitrogen. To aid the heat transfer process, the 2 cm diameter glass was flattened into a 0.7 cm wide by 2.0 cm deep rectangular section which was 27 cm long. The reboiler was heated by mineral insulated electrical type and a temperature controller was utilized to maintain heater temperature at about 200°C. Immediately below the reboiler was a 0.7 cm diameter x 10 cm long bottom seal leg.

B.3 Solids Flow Control/Lift Systems

Initially the bottom seal leg extended down to the carrier gas line. However, this arrangement did not allow solids flow rate control. After some experimentation, modifications were made to the seal leg as shown in Figure 1. Initially, the portion between the vertical legs of the seal leg was horizontal. Addition of a 20° slope allowed higher solids flow rates.

Solids flow rate control was effected initially by varying the amount of solids feed gas. However, a vibrator controlled by a variable power supply produced improved performance over a wide solids flow rate range. The flow rate was monitored by timing the movement of particles down the column.

The solid adsorbent was pneumatically returned to the top of the column with nitrogen gas (approximately 18 L/min) which was metered with a mass flow meter. A cooler was installed in the solids lift line to remove heat introduced into the solids at the reboiler.

B.4 Solids Disengager/Fines Collection System

Solids were removed from the lift gas at the top of the apparatus by a disengager. The disengager was 10 cm in diameter and 20 cm high with a 5 cm high conical section. A port was provided at the top to allow introduction of the adsorbent. Fines carried over from the disengager are removed by an all glass cyclone. The diameter of the cyclone was 5 cm and it was constructed as recommended by Perry/9/. However, the gas inlet was 0.7 cm in diameter instead of rectangular. Gas from the cyclone was directed onto a water surface in a flask to knock out very fine material and thence to vent.

B.5 Operating Procedure

Start-up of the system consisted of turning on the carrier gas (nitrogen) flow at about 18 L/min, the water flow to the cooling jacket on the solids lift line and the reboiler heater. Then, the vibrator was started and adjusted to produce the desired solids velocity down the column. The bottom product port was sampled after 10 min to ensure no oxygen was present and the hydrogen isotope feed to the system started. Adjustments were made to the bottom product flow valve and the disengager pressure. This latter was controlled by a valve at the vent line to be high enough such that nitrogen flowed up the reboiler and down the top seal leg. This ensured that hydrogen exited the column at the top and bottom ports only. Steady state compositions were obtained after about one to two hours but could be longer if the column initially had no hydrogen content and if the feed rate was low. The column was shut down by discontinuing the hydrogen feed and the nitrogen carrier gas and closing all ports to prevent oxygen entry.

APPENDIX C

Calculations

C.1 HTU Calculations from Bench Scale Data

The experimental data are shown in Tables 1 and 2. The number of transfer units was calculated as follows. Additional details may be found in Reference 10. The equilibrium curve was obtained from the expression $x_e = y_e / [\alpha - (\alpha - 1) y_e]$ where x_e is the mole fraction of D_2 in the solid phase, and y_e is the mole fraction of D_2 in the gas phase. The separation factor, α, is 1.91/3/ for low values of the D_2 concentration and 2.0 at about 30% D_2. The bottom product operating line was calculated from the bottom product flow (B) the bottom product composition (y_{BP}) and the "liquid" rate down the column. This latter (L) is given by:

L = (solids velocity) X (column area) X (untapped bulk density of adsorbent) X (palladium content of adsorbent) X (hydrogen absorbing capacity per gram of palladium)

Hence, using a mass balance on the deuterium content, the bottom section operating line is given by:

$$y = \frac{L}{L-B} . x \quad - \quad \frac{B}{L-B} \cdot y_{BP}$$

where y is the deuterium concentration in the gas phase and x the deuterium concentration in the solid phase.

Similarly, for the top section, the operating line is given by:

$$y = \frac{L}{L+T} \cdot x + \frac{T}{L+T} \cdot y_{TP}$$

where T is the top product hydrogen isotopes flow.

The number of transfer units is given by

$$NTU = \int_{y_{BP}}^{y_{TP}} \frac{dy}{y_e - y}$$

where y_{TP} and y_{BP} are the experimentally found gas phase deuterium concentrations in the top and bottom products, respectively. The value of y_e was obtained for a given y by substituting into the equations for the operating and equilibrium lines.

The NTU was obtained by calculating the area under the $1/(y_e-y)$ vs y curve on a computer. Hence, the height of a transfer unit is the column length divided by the number of transfer units.

C.2 **Full Scale Plant Calculations**

The following conditions were used to calculate the size of the column for a 200 L/d full scale plant:

Column temperature: 50°C

Separation factor: α = 2.5 + mole fraction tritium/4/

Solids velocity: 12 cm/min

Untapped bulk density of adsorbent: 1.21 g/cm^3 at 25% Pd on Al_2O_3

Column capacity: 240 mL/min/cm^2

APPENDIX D

Preliminary Cost Estimate

Because palladium is an expensive material, preliminary costs were calculated for a 200 L/day detritiation plant to determine if the experimental work was warranted. The Russian data/3/ were used. Similar palladium requirements for H/T separation as compared to H/D separation were assumed together with a column capacity of 300 mL (NTP)/min/cm^2 hydrogen feed as used by Andreev et al/3/. This corresponds to a velocity of 5 cm/sec and resulted in a single column of diameter 25 cm or four parallel columns each of diameter 12.5 cm. The number of transfer units was assumed to be similar to the number of theoretical plates which at total reflux is given by:

$$N = \frac{\log \left[\left\{ \frac{\text{mole fraction tritium}}{\text{mole fraction protium}} \text{ in Top Product} \right\} \times \left\{ \frac{\text{mole fraction protium}}{\text{mole fraction tritium}} \text{ in Bottom Product} \right\} \right]}{\log \alpha_{\text{average}}}$$

For the top and bottom product compositions desired, and with an average separation factor of three/3/, the number of plates at total reflux was calculated to be 20. This value was doubled to allow for product take-off. The height of a transfer unit was assumed to be 3 cm and the palladium bulk density 4.6 g/cm^3. The amount of palladium was increased by 15% to allow for material at the top and bottom of the column. Assuming a \$6,400 Cdn/kg (\$200/oz) palladium market cost with an additional 15% for processing the palladium into a suitable substrate, the total cost of palladium was calculated to be about \$2.5 x 10^6 (1985).

It was estimated by Sood/8/ that for a sorption process to be competitive with cryogenic distillation for coolant processing, the lifetime cost of the adsorbent should be approximately \$3 x 10^6 (1985). While the above palladium cost estimate is very similar to this value, it was felt that experimental work was warranted. This was because it was thought that the centres of pure palladium particles may not be utilized and the palladium requirement could be reduced if it were dispersed on a substrate. Also, the price of palladium fluctuates considerably with the mid-1985 market price being \$190 Cdn/oz. The late 1985 price being \$130/oz and present price of about \$150/oz.

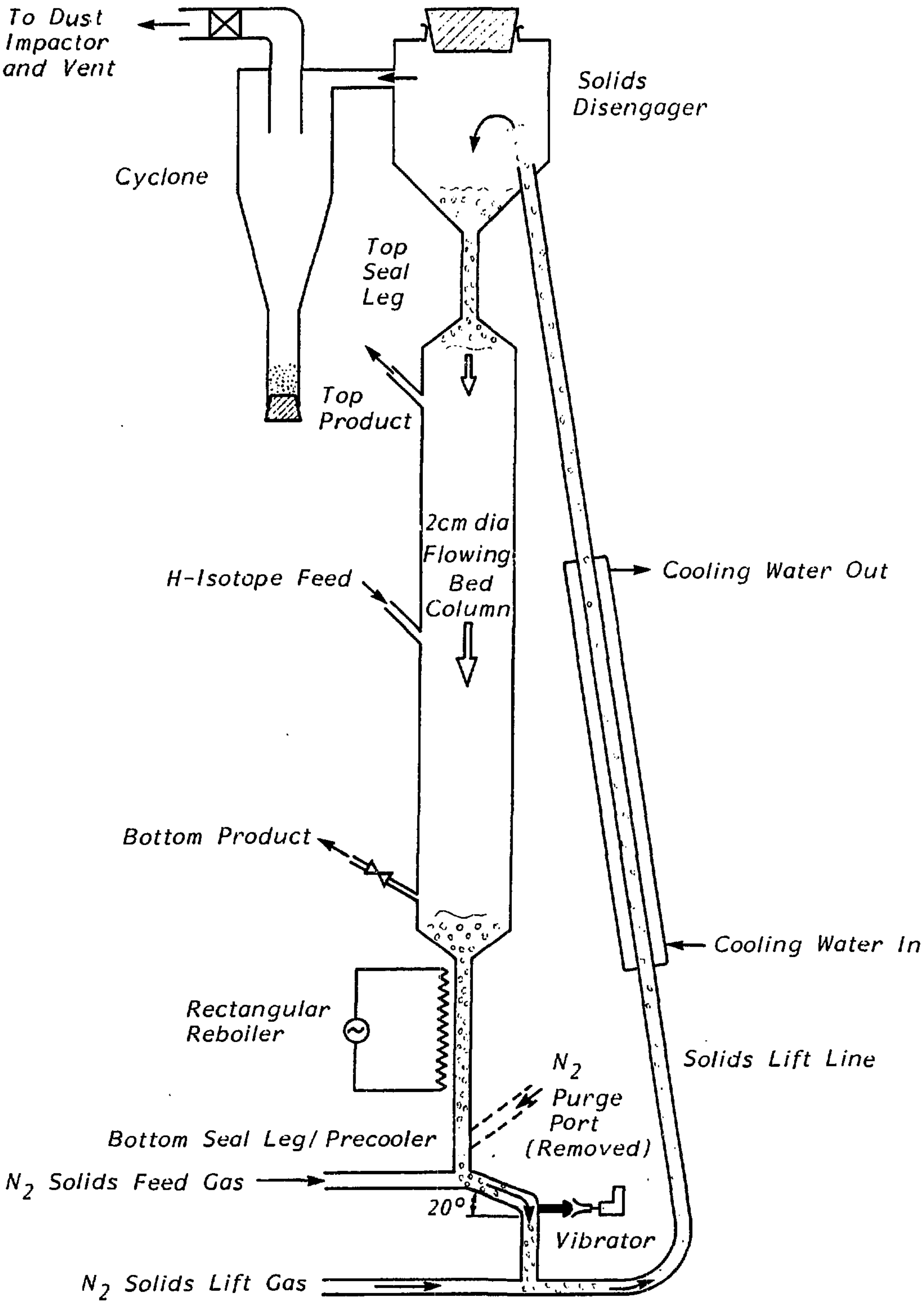

FIGURE 1

SCHEMATIC OF FLOWING BED APPARATUS

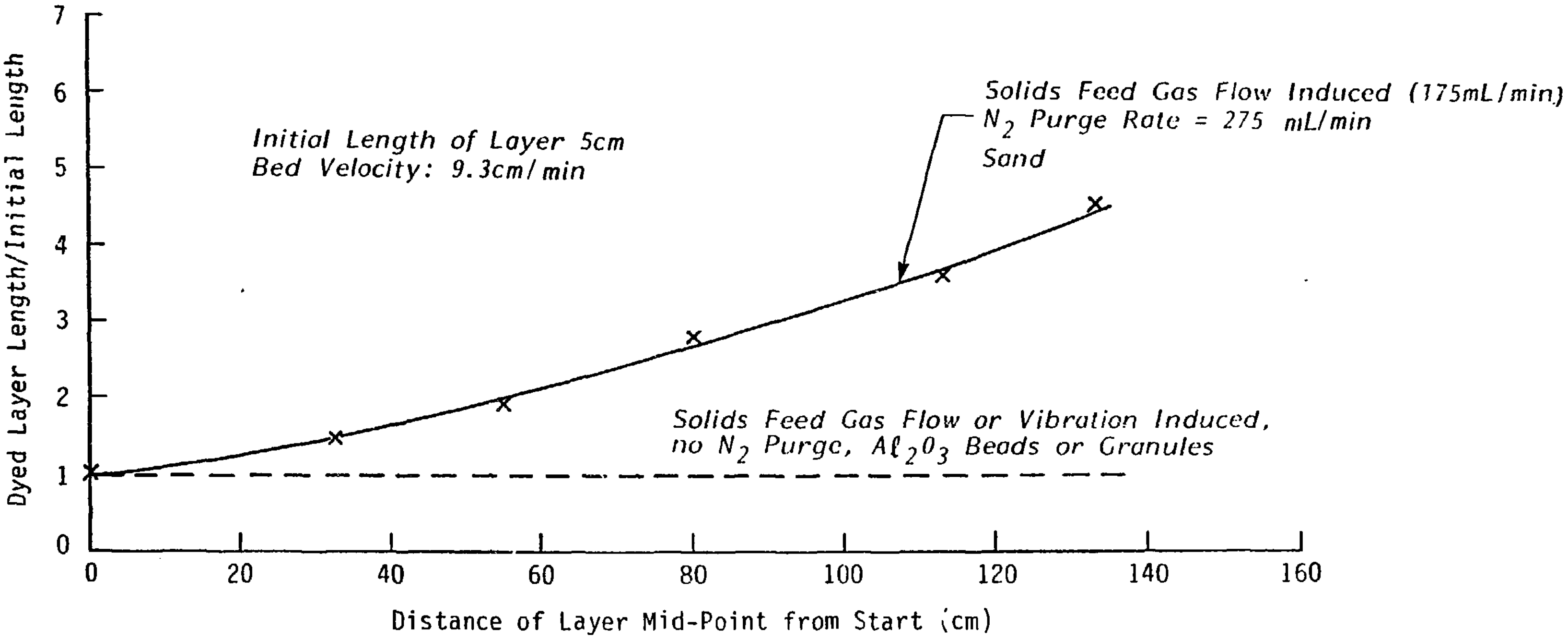

FIGURE 2

DISPERSION CHARACTERISTICS OF DYED LAYERS MOVING DOWN THE COLUMN

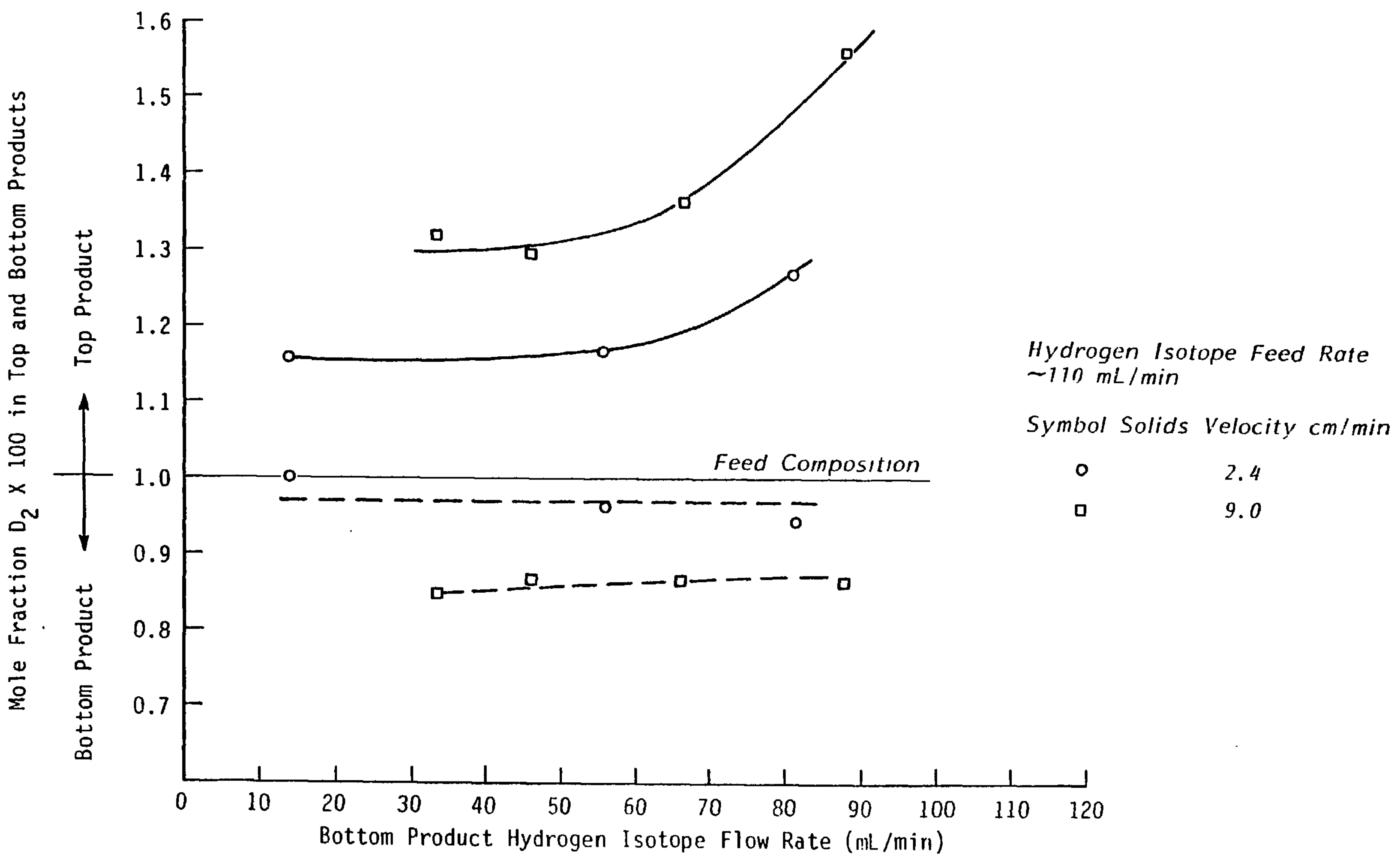

FIGURE 3

EFFECTS OF BOTTOM PRODUCT FLOW RATE AND SOLIDS VELOCITY

Table 1. Separation Performance Data

Test Number	Hydrogen Isotope Flows (mL/min at NTP)			Composition $\left\{\frac{\text{moles } D_2}{\text{moles } D_2 + \text{moles } H_2}\right\}$			Solids Velocity (cm/min)	NTU Overall	NTU Bottom Section	HTU Overall (cm)	HTU Bottom Section (cm)	HTU Top Section (cm)
	Feed	Top Product	Bottom Product	Top Product	Feed	Bottom Product						
44	1010	45.5	960	0.0153	0.01	0.0094	12.3	1.016	0.105	143	714	77
43	350	189	170	0.0117	"	0.0080	"	0.805	0.458	180	164	201
42	"	108	253	0.0122	"	0.0084	"	0.783	0.352	185	213	162
41	"	297	51.4	0.0105	"	0.0084	"	0.474	0.366	306	205	650
33	100	32.2	62.8	0.519	0.30	0.24	"	2.014	0.524	72	143	47
31*	125	81.1	46.6	0.0145	0.01	0.0075	10.4	1.411	0.604	103	124	87
30	125	63.1	59.0	0.0149	"	0.0088	11.2	1.129	0.268	128	280	81
29(i)	110	59.0	46.8	0.0129	"	0.0087	9.0	0.836	0.288	173	260	128
(ii)	"	58.0	48.7	0.0131	"	0.0085	"	0.922	0.340	157	220	120
(iii)	"	54.6	50.4	0.0129	"	0.0086	"	0.864	0.315	168	238	128
(iv)	"	20.1	88.3	0.0157	"	0.0086	"	1.274	0.312	114	240	73
(v)	"	37.2	66.7	0.0136	"	0.0086	"	0.972	0.315	150	238	107
(vi)	"	68.1	32.6	0.0132	"	0.0084	"	0.968	0.367	150	204	116
(vii)	"	68.4	32.2	0.0130	"	0.0082	"	0.985	0.416	147	180	123
28(i)	95	9.15	83.0	0.0165	"	0.0096	14.2	1.147	0.0848	126	884	70
(ii)	100	66.1	42.6	0.0142	"	0.0090	9.2	0.982	0.220	148	341	92
25(i)	95	81.8	13.0	0.0116	"	0.0100	2.4	0.348	0	417	∞	201
(ii)	"	37.3	56.0	0.0116	"	0.0096	"	0.410	0.0808	353	928	212
(iii)	"	14.4	81.7	0.0127	"	0.0094	"	0.634	0.119	229	630	136
(iv)	"	59.8	72.8	0.0124	"	0.0100	6.0	0.470	0	309	∞	149

NTP = 25°C, 101.325 kPa

* Helium carrier gas, all other tests used nitrogen

Table 2. Column Temperatures, Nitrogen Flows and Column Pressures During Performance Testing

Test Number	Average Column Temperature (°C)	Nitrogen Flows (mL/min)			Column Pressures (inches H_2O)					Comments
		Carrier Gas	Top Product	Bottom Product	Carrier Gas	Bottom Product	Feed	Top Product	Disengager-Top Product	
44	~50	19 100	113	67	15.9	11.3	11.5	8.8	0.5	
43	"	19 000	584	6.3	11.0	6.0	4.6	0.7	4	
42	"	"	725	22.0	11.3	6.8	5.0	0.3	4.3	
41	"	17 400	698	1.4	11.6	8.3	6.0	0.6	4.8	
33	"	17 500	620	1.3	10.6	7.3	4.5	0.4	4.1	
31	"	22 500	719	5.4	9.7	6.4	4.0	0.1	4	Helium not N_2
30	~75	17 000	552	2.0	9.7	6.9	4.5	0.1	4	
29(i)	~50	17 200	424	2.2	7.6	5.4	4.5	0.1	3	
(ii)	"	"	563	4.3	8.5	6.1	4.1	0.1	4	
(iii)	"	"	695	5.6	9.9	7.0	4.6	0.2	5	
(iv)	"	"	520	6.8	8.6	6.1	4.2	0.1	4	
(v)	"	"	507	4.3	8.8	6.2	4.3	0.1	4	
(vi)	"	"	487	1.4	8.7	6.4	4.5	0.1	4	
(vii)	"	"	487	2.0	8.7	6.4	4.5	0.1	4	
28(i)	~60	"	627	3.0	9.9	6.8	4.5	0.2	4	
(ii)	"	"	574	2.4	9.9	6.5	4.5	0.2	4	
25(i)	~30	17 100	130	4.3	4.4	3.3	2.5	1.3	0.5	
(ii)	"	"	148	23.4	4.5	3.1	2.4	1.2	0.5	
(iii)	"	"	125	36.3	4.5	3.0	2.3	1.2	0.5	
(iv)	~40	"	58.2	1.1	5.6	4.2	3.0	1.4	0.5	

Table 3. Stationary Bed Flushing Test Data

Form of Palladium Adsorbent	Gas Mixture Loaded on Adsorbent (mole fraction D_2 in H_2)	Flush Gas Composition (mole fraction D_2)	Flush Gas Rate* {Solids Velocity Equivalent (cm/min)}	Time Period Over Which Flushing Performed (min)	Estimated** Column Length Required (cm)	Effluent D_2 Concentration at End of Flush Period (mole fraction D_2)
Al_2O_3 impregnated with Pd in pores; 25% by weight Pd	0.01	0	1.7	13.5 18.25	23 30	0.005 0.001
Physical mixture of pure Pd particles and Al_2O_3 spheres; 25% by weight Pd	0.01	0	2.3	3.0	8	0.001

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* H_2 capacity = 100 mL (NTP/g 25% Pd/Al_2O_3 adsorbent (the Al_2O_3 substrate exhibited negligible H_2 adsorption)

** Column length = solids velocity equivalent of flush gas rate x time period over which flushing performed

Table 4. Estimated Costs of Moving Bed Systems for Various Adsorbents

Factor	Comments	Relative Importance of Factor (RIF) on Overall Costs	Effect of Factor on Cost Relative to Average (CRA) for All Adsorbents				
			25% Palladium on Alumina	Molecular Sieve	Vanadium	Uranium	FeTi
1) Separation factor	Determines column height.	low	very low	average	high	average	very high
2) Capacity for hydrogen	Determines column diameter. Small diameter promotes plug flow down column.	average	high	average	low	average	average
3) Adsorbent inventory	Determines initial material costs.	average	very high	low	average	high	low
4) Promotion of isotopic equilibration	Avoids additional processing and equipment.	average	low to avg	very high	low to avg	low to avg	low to avg
5) Operating temperature	Near ambient desirable.	average	very low	very high	average	average	average
6) Operating pressure	Complexity increases above atmospheric pressure.	average	average	average	average	average	average
7) Availability of suitable adsorbent form	~1 mm preferred for pneumatic conveying. Spherical shape desirable.	low	avg to high	very low	avg to high	avg to high	avg to high
8) Direction of tritium movement	Downward tritium movement increases potential for carrier gas decontamination requiring carrier gas clean-up equipment.	average	low	very high	very high	low	low
9) Resistance to poisoning	Determines adsorbent make-up cost	average	low	very low	high	high	high
10) Resistance to powdering	Determines adsorbent make-up costs and scrubbing equipment provision	high	average	very low	high	high to very high	high
Overall Costs $\sum_{i=1}^{i=10} (RIF)_i \times (CRA)_i$			80	84	99	95	92